

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
4 October 2001 (04.10.2001)

PCT

(10) International Publication Number
WO 01/73153 A1

- (51) International Patent Classification⁷: **C23C 14/16**
- (21) International Application Number: **PCT/GB01/01407**
- (22) International Filing Date: **27 March 2001 (27.03.2001)**
- (25) Filing Language: **English**
- (26) Publication Language: **English**
- (30) Priority Data:
0007559.8 29 March 2000 (29.03.2000) GB
0010246.7 28 April 2000 (28.04.2000) GB
0030465.9 14 December 2000 (14.12.2000) GB
- (71) Applicant (*for all designated States except US*): **TRIKON HOLDINGS LIMITED** [GB/GB]; Coed Rhedyn, Ringland Way, Newport, Gwent NP18 2TA (GB).
- (72) Inventors; and
- (75) Inventors/Applicants (*for US only*): **RICH, Paul** [GB/GB]; 109 Parklands, Wotton-Under-Edge, Gloucestershire GL12 7NR (GB). **HARRIS, Mark, Graeme, Martin** [GB/GB]; 6 Roman Reach, Caerleon, Newport NP18 3SG (GB).
- (74) Agents: **DUNLOP, Brian, Kenneth, Charles et al.**; Wynne-Jones, Laine & James, 22 Rodney Road, Cheltenham, Gloucestershire GL50 1JJ (GB).
- (81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.
- (84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, R, NE, SN, TD, TG).

Published:

— with international search report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: **METHOD OF DEPOSITING METAL FILMS**

(57) Abstract: The invention relates to methods of sputter deposition of a metallic layer on to a substrate including utilising substantially krypton.

WO 01/73153 A1

comparatively little researched. The alternative, proposed in the prior art is to sputter with xenon, a gas that costs approximately 25,000 times more than sputter grade argon.

5 In physical vapour deposition processes e.g. sputtering it is widely known that increasing the substrate temperature improves film quality and as a result almost all sputtering processes are onto substrates heated to typically over 150°C and frequently much higher.

10 These high temperatures in general present no problem to the substrate. However there is a process procedure known as 'lift-off' where a resist pattern (typically organic) is created and then the chosen material deposited onto the thus patterned substrate surface. After deposition the

15 resist is 'lifted off' by e.g. use of solvent, removing not only the resist but also the material deposited upon it thus leaving a pattern of deposited material. This technique avoids the use of an etchant for the deposited material and is a method of choice for noble metals for

20 obvious reasons however temperatures of over 100-120°C damage the resist and therefore this represents a maximum substrate temperature severely limiting standard substrate heating procedures for improving the electrical properties of deposited metals.

25 The prior art relating to the choice of sputter gas consists in three parts. Firstly that there are several possible gasses for use in sputtering, being the noble

From another aspect the invention consists in a method of depositing a noble metal on to a substrate comprising sputtering of the metal utilising a process gas characterised in that the process gas is at least predominately krypton.

Description of embodiments

To illustrate the effect of substrate temperature with noble metal deposition a gold sputtering process using argon has been run onto semiconductor wafers. The gold, when deposited for 1 minute on wafers at low temperatures (platen temperature of 50°C), was of 4.5 micro ohm cm. resistivity and was of 2.5 micro ohm cm. resistivity when deposited for 1 minute on warm wafers (a platen temperature of 150°C) all other process conditions identical.

Thus where low substrate temperatures are a requirement a novel process producing a high electrical quality metal layer (e.g. low resistivity) is needed. These low temperatures may be required where the substrates are coated with organic layers damaged by temperatures typical of metal deposition processes. These organic layers could be for example lift-off resist patterns or organic containing low-k dielectric materials e.g. carbon or methyl doped silicon dioxide.

Krypton and Argon were experimented with in a Gold deposition process giving the following results:

In addition to the experiments described in the above the following further experiments have been carried out with a range of gasses to sputter gold. The results are as follows:

5 Process conditions:

Silicon wafer substrate

1kW target power

2min process time

-16°C wafer platen temperature

Sputter Gas	Resistivity $\mu\Omega\text{cm}$	Sheet Resistance Ω/\square	Thickness \AA	DC Target Voltage	Process Pressure millitorr
Neon	14.9	1.49	1000	427	3.5
Argon	5.2	0.322	1600	559	3.5
15 Krypton	2.6	0.155	1700	745	3.5
Xenon	2.8	0.255	1100	785	20

The gasses experimented with are all the non-radioactive noble gasses.

It may be that a key aspect of Gold layer resistivity on a substrate is sputter gas inclusion in the sputtered film during the sputtering process. Krypton may include less than argon due to its larger size. If this explanation is correct then it would be expected that xenon would yield even better electrical quality metal layers for any given applied target power, substrate temperature and pressure.

consumed. This renders the process 30 times more costly in gas consumption. By way of contrast argon of the same quality in bulk costs over 5,000 times less than krypton. A typical sputter process might use 0.2 litres of argon per wafer. At the time of writing therefore the sputter gas cost per semiconductor wafer would rise from 0.001 pence per wafer for argon to 53 pence per wafer for krypton and £14.29 per wafer for xenon.

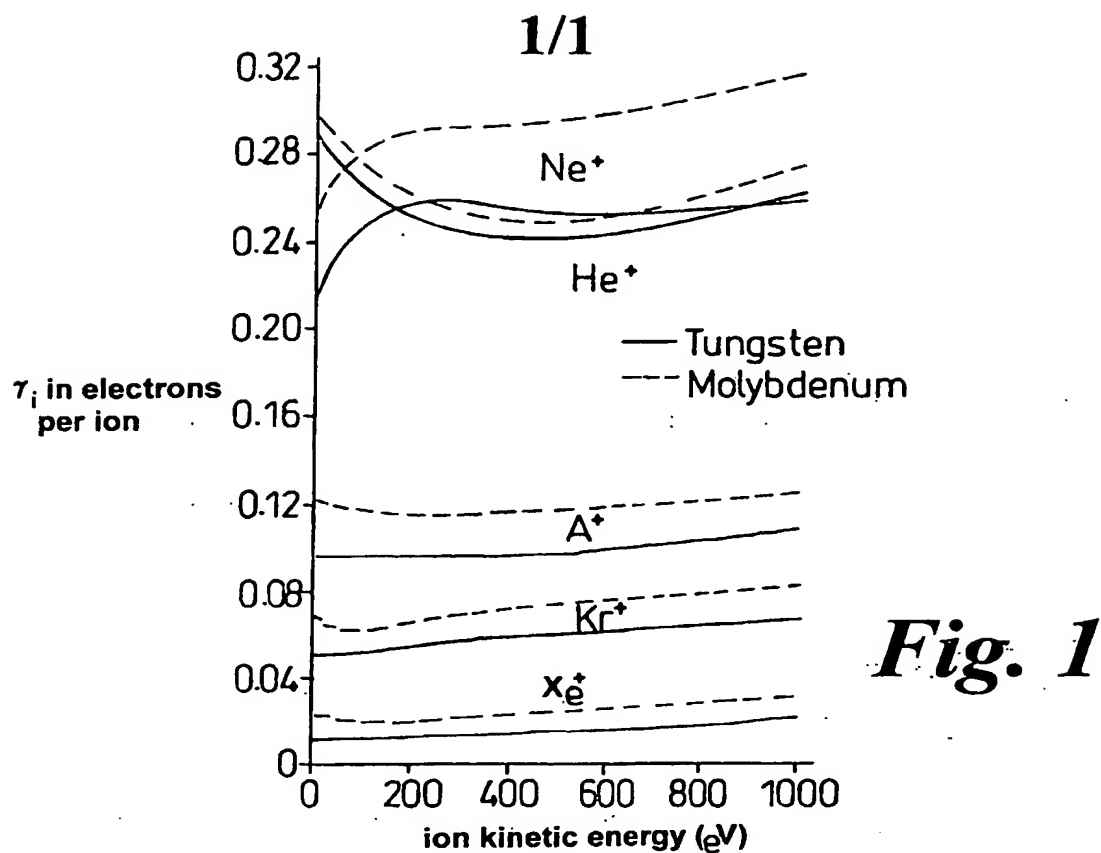
This increase in pressure can also be achieved by reducing the pumping speed. Whilst this avoids the increase in gas consumption, it offers no other benefit and is generally considered undesirable.. All vacuum systems leak slightly and the substrates outgas absorbed gasses. Reducing the pumping speed increases the proportion of this gas contamination in the sputter gas thus further reducing sputtered film quality.

It should also be noted that for a given process time and applied power the sputtered thickness was less for xenon than for krypton, at least in part due to increased gas scattering in the higher pressure gas. In effect the target has been sputter eroded, but the sputtered material is wasted on the chamber wall shielding rather than being deposited onto the substrate. This is significant with a target as valuable as e.g. gold or platinum. As can be seen in the experimental results krypton was 54.5% more efficient than xenon at depositing gold onto the substrate

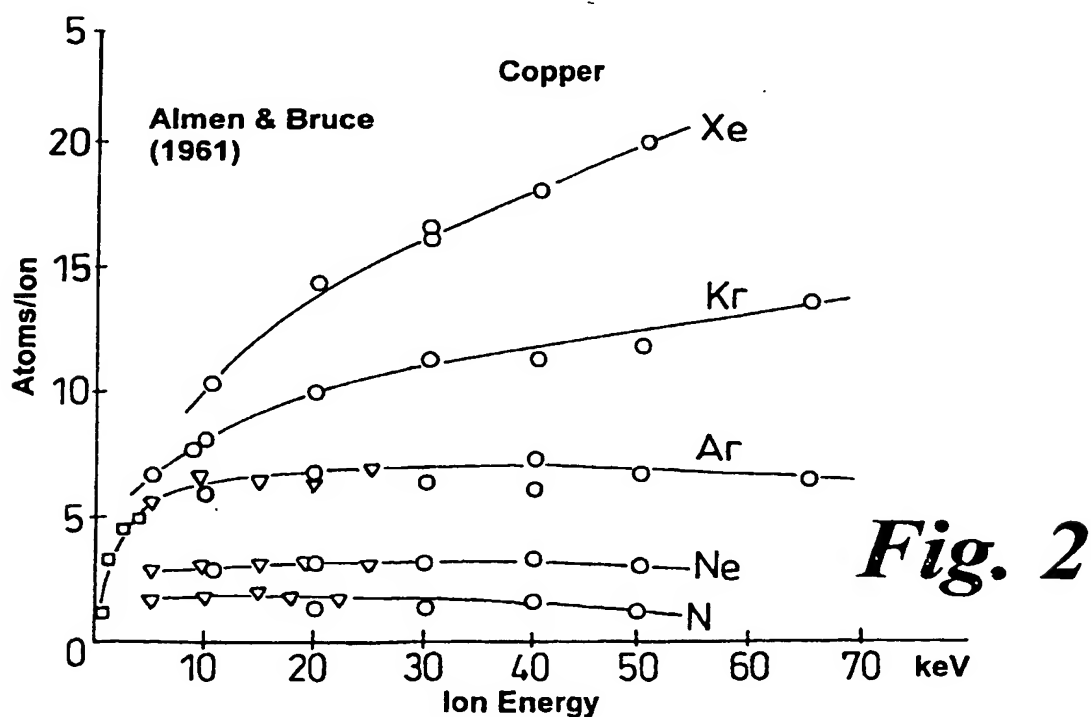
It should be understood that the advantage of using krypton shown here will attach to mixes of krypton and another noble gas and any effective improvement by the inclusion of krypton is to be included in the this invention.

It should also be understood that this invention is particularly advantageous where the substrate, for example a compound semiconductor wafer perhaps with an organic mask in place or any semiconductor wafer with a low thermal budget, cannot be heated to an effective temperature to reduce the sputtered film resistivity when using argon. This invention can thus be seen as a way of reducing process temperature to achieve the same resistivity sputtered films.

An electrostatic chuck may advantageously be used to improve platen to substrate thermal transfer enabling more effective temperature control of the wafer. The electrostatic chuck may be chilled to below ambient temperatures.



Secondary electron yields γ_i for noble gas ions on atomically clean tungsten and molybdenum (Hagstrum 1956b)



Sputtering yields of the noble gases on copper, as a function of energy (Almen and Bruce 1961)

INTERNATIONAL SEARCH REPORT

International Application No
GB 01/01407

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 068 022 A (CARCIA PETER F) 26 November 1991 (1991-11-26) examples 1-9 ---	1,2,7
X	US 5 403 629 A (EICHMANN WOLFGANG ET AL) 4 April 1995 (1995-04-04) claims 1-4 ---	1,2,7
X	PATTEN J W ET AL: "Krypton bubble formation and growth in sputtered gold" INTERNATIONAL CONFERENCE ON METALLURGICAL COATINGS, SAN DIEGO, CA, USA, 21-25 APRIL 1980, vol. 72, no. 2, pages 361-372, XP001002892 Thin Solid Films, 1 Oct. 1980, Switzerland ISSN: 0040-6090 paragraph '0002! ---	1-3
Y	DATABASE WPI Section Ch, Week 199242 Derwent Publications Ltd., London, GB; Class A89, AN 1992-345763 XP002169824 & JP 04 251453 A (TAIYO YUDEN KK), 7 September 1992 (1992-09-07) abstract -----	6